# Supporting Information

## Visible Light Sensitized $CO_2$ Activation by the Tetraaza $[Co^{II}N_4H(MeCN)]^{2+}$ Complex Investigated by FT-IR Spectroscopy and DFT Calculations

M. Zhang[a], M. El-Roz[a,b], and H. Frei*

*Physical Biosciences Division and Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

J. L. Mendoza-Cortes[a] and M. Head-Gordon*

*Chemical Sciences Division and Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

D. C. Lacy and J. C. Peters*

*Division of Chemistry and Chemical Engineering, and Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, California 91125, United States*

HMFrei@lbl.gov, Ph 510-486-4325, Fax 510-486-4995
MHead-Gordon@cchem.berkeley.edu, Ph 510-642-5957, Fax 510-643-1255
JPeters@caltech.edu, Ph 626-395-4036, Fax 626-395-6948

[a] Authors contributed equally
[b] Permanent address: Laboratoire Catalyse et Spectrochimie, ENSICAEN-Universite de Caen-CNRS, France

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# 1 Further details on the spectroscopic experimental methodology

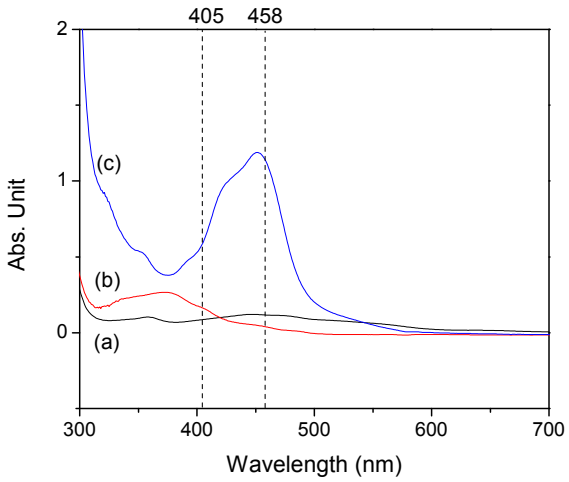


Figure S1: The UV-vis absorption spectra of (a) $[Co\mathbf{N_4H}(MeCN)]^{+2}$ catalyst (1 mM solution in acetonitrile), (b) photosensitizer Ir(III)$(ppy)_3$ (0.2 mM solution in acetonitrile) and (c) photosensitizer Ru(II)$(bpy)_3$ (1 mM solution in acetonitrile). The spectra were collected by a Shimazu SolidSpec-3700 UV-vis spectrometer with a 1 mm quartz cell.

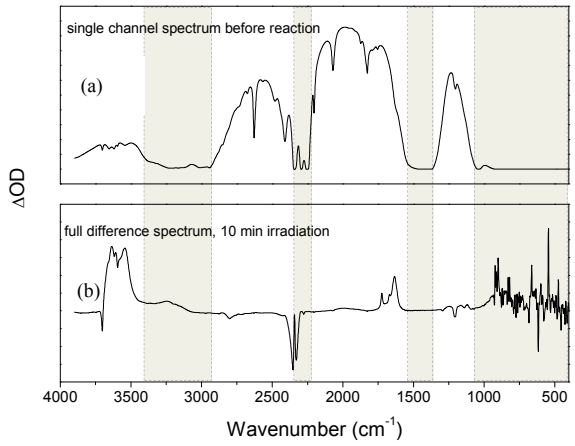


Figure S2: (a) The single channel spectrum of the sample contains $[Co\mathbf{N_4H}(MeCN)]^{+2}$ 1 mM, Ir(III)$(ppy)_3$ 0.2 mM, TEA 0.1 M and $CO_2$ in acetonitrile solution before illumination. (b) The difference spectrum of the sample after 10 min illumination with a 405 nm laser (170 mW). The difference spectrum was obtained by dividing the spectrum after 10 min photolysis with the spectrum before reaction. The windows in gray are blocked by the solvent absorption according to the single channel spectrum, since there is no light pass through at these regions. The window between 2200 $cm^{-1}$ to 1550 $cm^{-1}$ is the most interesting one in all the open windows in this study.

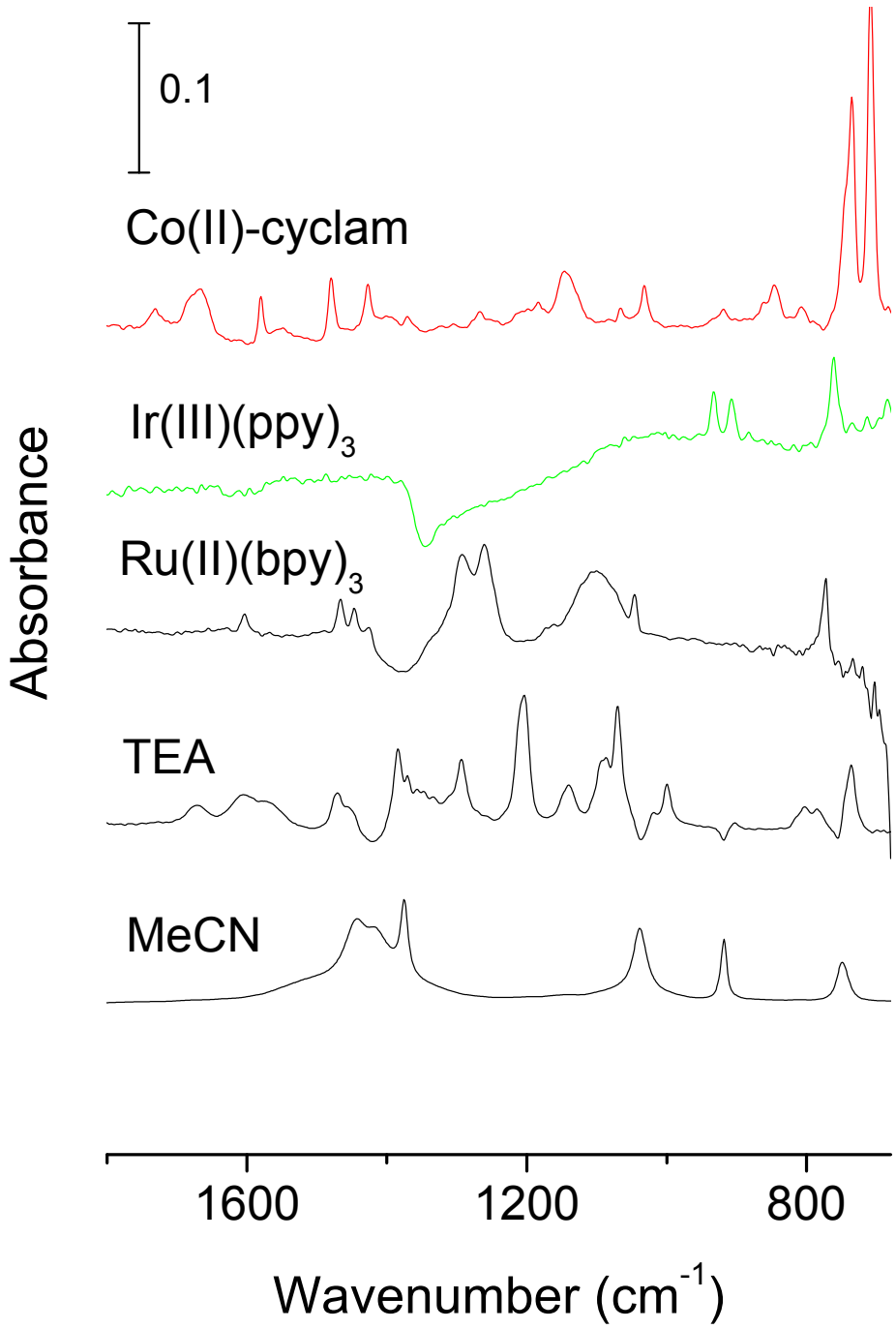


Figure S3: The FTIR spectra of the chemicals used in this work. The spectra were taken with Bruker Vertex 80 spectrometer equipped with an ATR accessory with a 3 mm diamond plate.

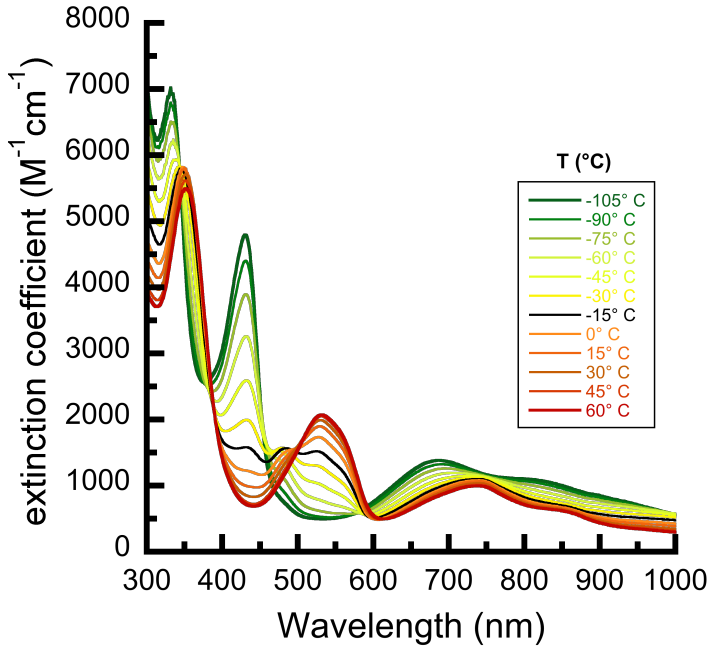


Figure S4: (a) Variable temperature UV-vis spectrum of 0.3 mM $[Co\mathbf{N_4H}(MeCN)]^+$ in Tetrahydrofuran (THF) with 10 M $H_2O$. Spectra were collected with a Cary 50 spectrometer equipped with an Unisoku cryostat. The spectral traces indicate the conversion of the 5-coordinate $[Co\mathbf{N_4H}(MeCN)]^+$ complex at low temperature (green) to 4-coordinate $[Co\mathbf{N_4H}]^+$ complex at high temperature (red) upon MeCN ligand dissociation

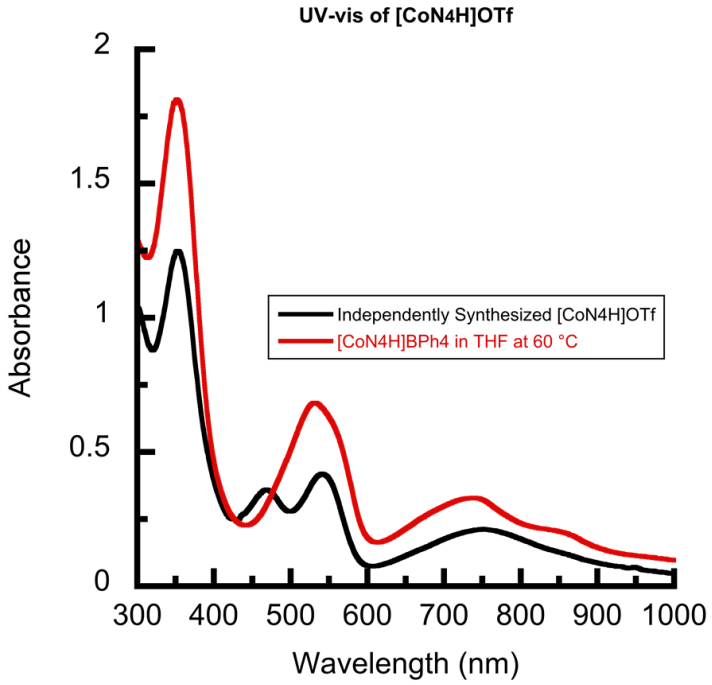


Figure S4: (b) UV-vis spectrum of independently synthesized 4-coordinate $[Co\mathbf{N_4H}]OTf$ in THF (black) compared to $[Co\mathbf{N_4H}]BPh_4$ formed upon dissociation of $[Co\mathbf{N_4H}(MeCN)]BPh_4$ in THF at 60 °C (red, see Figure S4a). The spectral agreement confirms the 4-coordinate geometry of the dissociated complex.

# 2 Preparation and characterization of the $[CoN_4H]OTf$

## 2.1 Preparation

A solution of [Co**N$_4$**] (170 mg, 0.540 mmol) in 10 mL of THF was treated dropwise with [H·DMF]OTf (118 mg, 0.530 mmol) dissolved in 1 mL THF. Addition caused effervescence and the solution warmed, presumably from the reaction of the acid with newly formed [Co**N$_4$H**]OTf. The resulting dark purple solution was concentrated to about 3/4 original volume and filtered through a medium porosity glass-fritted funnel to obtain 107 mg of dark purple crystals of [Co**N$_4$H**]OTf (43% yield). A $^1$H-NMR spectrum of the crystals in $d_3$-MeCN were identical to the [Co**N$_4$H**(MeCN)][$BPh_4$] salt except that no peaks associated with the tetraphenyl borate anion were present.[1] UV-vis: $\lambda_{max}$, nm ($\epsilon$, $M^{-1}cm^{-1}$) 354 (5650); 467 (1630); 541 (1916); 749 (966).

## 2.2 Crystallography

The red-purple filtrate of the crude reaction mixture produced crystals suitable for diffraction upon standing at room temperature. XRD data was collected on either a Siemens or Bruker three-circle diffractometer with a Smart 1K CCD detector using Mo K$\alpha$ radiation ($\lambda$ = 0.71073), performing $\phi$-and $\omega$-scans and cooled with an Oxford Cryosystems crystal cooling system. The structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques using SHELX program package and Olex. All hydrogen atoms were located on the difference map and refined upon. [2, 3]

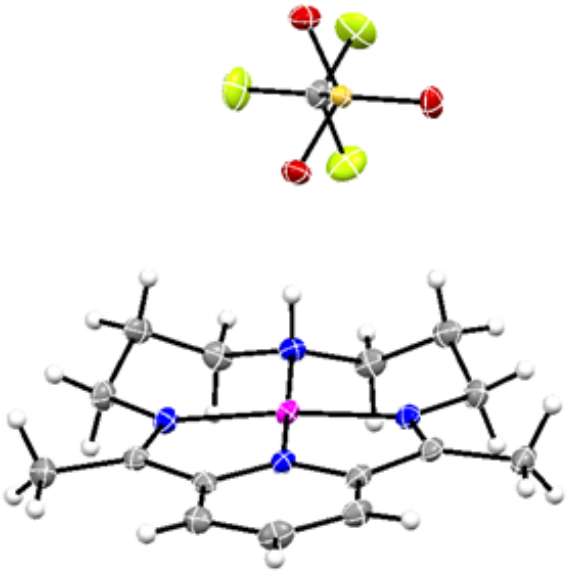

Figure S5: Thermal ellipsoid plot (50% probability) of the salt [Co**N$_4$H**]OTf.

Table S1: Crystal data and structure refinement for [Co**N$_4$H**]OTf.

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|---|---|
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| T (K) | 100 |
| crystal system | Monoclinic |
| space group | *P 21/c* |
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| $b$ (Å) | 13.0588(12) |
| $c$ (Å) | 16.670(2) |
| $\alpha$ (deg) | 90 |
| $\beta$ (deg) | 102.715(3) |
| $\gamma$ (deg) | 90 |
| Z | 4 |
| V (Å$^3$) | 1858.0(3) |
| $d_{calcd}$ (Mg/m$^3$) | 1.667 |
| Indep. Reflections | 3808 |
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## 2.3 Crystallographic information: cif file

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# checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

# Datablock: CoN4HOTf

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Bond precision:  C-C = 0.0029 A          Wavelength=0.71073

Cell:            a=8.7498(8)     b=13.0588(12)        c=16.670(2)
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Temperature:     100 K

                Calculated                Reported
Volume          1858.0(3)                 1858.0(3)
Space group     P 21/c                    P 1 21/c 1
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C15 H22 Co N4, C F3 O3 S  C15 H22 Co N4, C F3 O3 S
Sum formula     C16 H22 Co F3 N4 O3 S     C16 H22 Co F3 N4 O3 S
Mr              466.37                    466.37
Dx,g cm-3       1.667                     1.667
Z               4                         4
Mu (mm-1)       1.092                     1.092
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F000'           962.35
h,k,lmax        10,16,20                  10,16,20
Nref            3807                      3807
Tmin,Tmax       0.897,0.897               0.668,0.747
Tmin'           0.897

Correction method= MULTI-SCAN

Data completeness= 1.000          Theta(max)= 26.370

R(reflections)= 0.0264( 3419)     wR2(reflections)= 0.0645( 3807)

S = 1.043                 Npar= 341
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The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

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**Alert level C**

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PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.75 Report
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**Alert level G**

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PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         28 Report
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF     Please Do !
PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct.         21 Note
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Co01   --  N00B    ..        5.6 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Co01   --  N00C    ..        7.6 su
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........         48 Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          2 Note
              C F3 O3 S
PLAT793_ALERT_4_G The Model has Chirality at N00C    .............          S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         82 Note
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   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   9 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   4 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

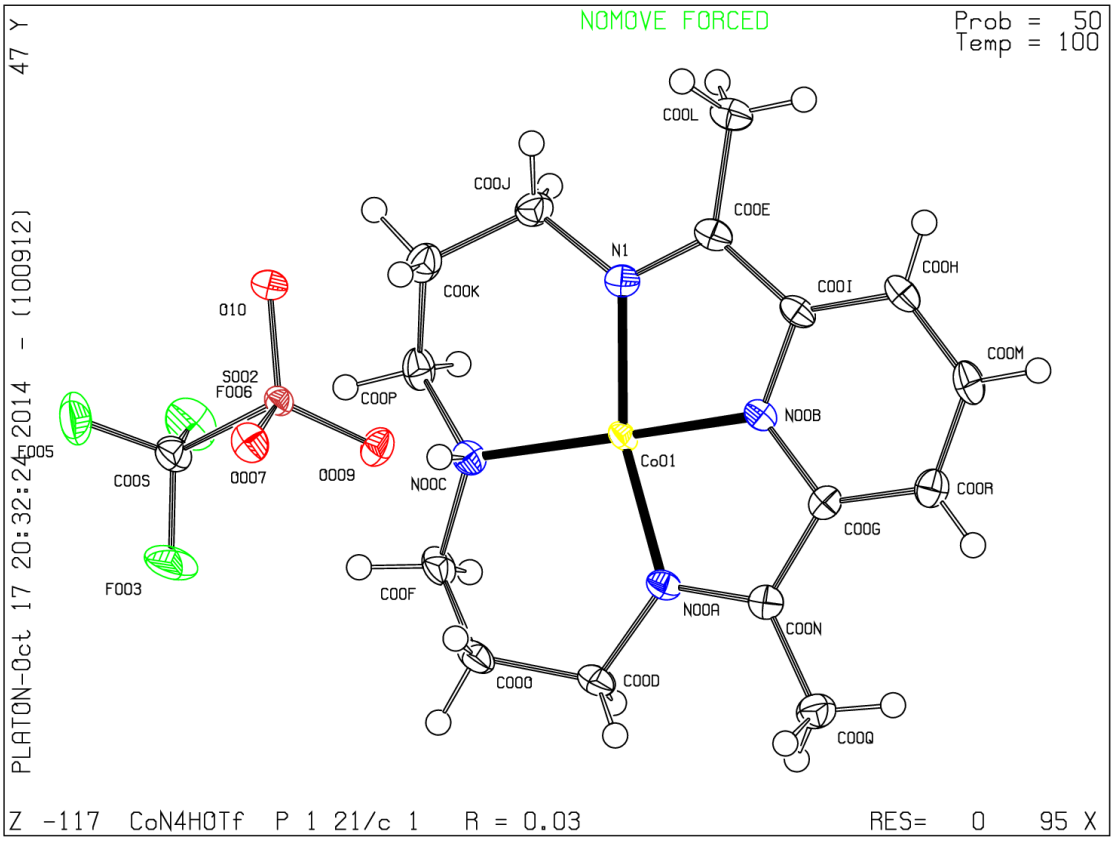
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

**PLATON version of 20/08/2014; check.def file version of 18/08/2014**

**Datablock CoN4HOTf** - ellipsoid plot



# 3 Further details on the computational methodology

Full geometry optimization calculation were performed at each of the levels of theory (BP86-D, PBE-D, B3LYP-D, and $\omega$B97X-D) as implemented in QChem v4.1.[4]. 6-31+G** basis set were used for the light elements and for the Co we used the Wachters basis set with f functions.[5, 6]

For some cases, we included solvation effects using the SWIG C-PCM approach ($CH_3CN$, $\epsilon = 35.9$, $\epsilon_\infty = 1.8$, $r_0 = 2.18$ from UFF). [7, 8] For this cases, free energies are calculated as:

$$G^{\text{solv}}_{298\text{ K}} = E_{\text{elec}} + G_{\text{solv}} + \text{ZPE} + H_{\text{vib}} - TS_{\text{vib}} \tag{1}$$

where we consider electronic (elec), solvation (solv), vibrational (vib), and zero point vibrational energy (ZPE).

Gas phase energies discussed in the text do not include solvation, thus the free energy expression is

$$G^{\text{gas phase}}_{298\text{ K}} = E_{\text{elec}} + \text{ZPE} + H_{\text{vib}} - TS_{\text{vib}} \tag{2}$$

The binding energies are defined as

$$\Delta G^{\text{bind}}_{298\text{ K}} = G(\text{catalyst} + \text{substrate}) - G(\text{substrate}) - G(\text{catalyst}) \tag{3}$$

e.g.

$$\Delta G^{\text{bind CO2}}_{298\text{ K}} = G(\text{catalyst} + CO_2) - G(CO_2) - G(\text{catalyst}) \tag{4}$$

# 4 Validation of functionals used for the DFT calculations

We validate the functional used for the screening of the binding modes by comparing the coordinates of the crystal structures versus the ones obtained from the different levels of DFT. We focus on the prediction of the Co-Nitrogen bonds inside the catalysts. We also compared the prediction of other bonds that potentially participate in the redox process (i.e. redox non-innocent). To make this comparison we used the Root Mean Square Deviation (RMSD) of experimental bond lengths ($L^{\exp}$) from the available crystal structure versus the bond lengths ($L^{\mathrm{DFT}}$) predicted by the functional. This is

$$\mathrm{RMSD} = \sqrt{\sum_{t=1}^{n} \frac{(L^{\exp} - L^{\mathrm{DFT}})^2}{n}} \tag{5}$$

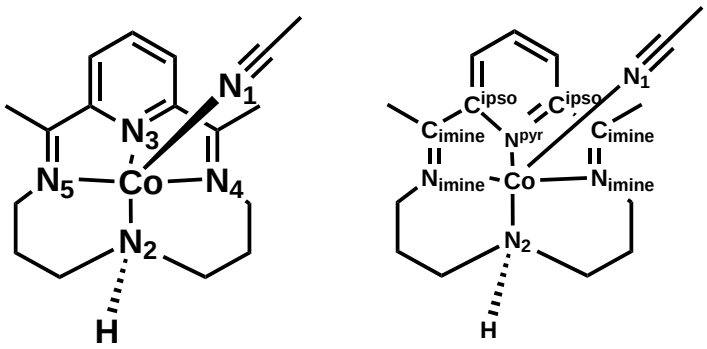



Figure S6: Labeling of the bonds for the different structures. We use the general connectivity to explain the naming. In the numeration table we used $r$ and $l$ to indicate the right and left side atoms, respectively.

**Notes**: The formal .cif files obtained from experiments is full with counter anions and with solvent molecules. For computational simplicity we remove the counter anions and also we studied the influence of the coordinated solvent molecule with different DFT functionals (See Figure 5 of main manuscript). A brief explanation of the simplification process follows.

- The experimental structure for $CoN_4$ (Table S2) does not contain solvent molecules or counter anions, thus no simplification was required.
- The experimental structure for the +2 species has the formula unit of $[Co^{(II)}N_4H(MeCN)](OTf)(BPh_4)$, however for the DFT calculation, we remove the counter anions and this species is called in the tables $CoN_4H(MeCN)^{+2}$ (Table S3). To study the binding energy of MeCN in gas phase and solvent, we remove the solvent in addition of the counter anions and create the $CoN_4H^{+2}$ (Table S4) geometry for our calculations. The intention was to quantify if the bound solvent molecule can be predicted better for different functionals (See Figure 5 of main manuscript).
- There are two experimental structures for the +1 species. For the so called $CoN_4H(MeCN)^{+}$ (Table S5) we used the crystal structure with formula: $[CoN_4H(MeCN)][BPh_4]$, where we remove the counter anions but not the bounded solvent molecule. For the so called $CoN_4H^{+}$ (Table S6) compound, we use the crystal structure from $[CoN_4H][OTf]$ without the counter anion, here the MeCN is not present, thus is ideal for the initial guess of the corresponding DFT calculations. Thus, the stability of bounded MeCN in the +2 species can also be studied (See Figure 5 of main manuscript).

Table S2: Bond length analysis for $CoN_4$ obtained from the different functionals. Bonds are given in Å

| $CoN_4$ | Crystal | B3LYP-D | | BP86-D | | PBE-D | | wB97X-D | |
|---|---|---|---|---|---|---|---|---|---|
| | | M1 | M3 | M1 | M3 | M1 | M3 | M1 | M3 |
| Co1-Npyr | 1.7997 | 1.8389 | 1.8704 | 1.8097 | 1.8556 | 1.8602 | 1.9128 | 1.8365 | 1.8690 |
| Co1-Nimine (r) | 1.8814 | 1.9280 | 1.9369 | 1.8925 | 1.8967 | 1.9621 | 1.9702 | 1.9327 | 1.9311 |
| Co1-Namine | 1.8096 | 1.8317 | 1.8531 | 1.8192 | 1.8444 | 1.8720 | 1.8967 | 1.8304 | 1.8448 |
| Co1-Nimine (l) | 1.8883 | 1.9275 | 1.9412 | 1.8918 | 1.9029 | 1.9615 | 1.9753 | 1.9323 | 1.9493 |
| Nimine-Cimine (r) | 1.3305 | 1.3254 | 1.3270 | 1.3468 | 1.3527 | 1.3646 | 1.3700 | 1.3133 | 1.3261 |
| Cimine -Cipso (r) | 1.4420 | 1.4448 | 1.4491 | 1.4365 | 1.4419 | 1.4651 | 1.4712 | 1.4494 | 1.4382 |
| Cipso-Npyr (r) | 1.3730 | 1.3748 | 1.3719 | 1.3891 | 1.3837 | 1.4141 | 1.4093 | 1.3688 | 1.3718 |
| Npyr-Cipso (l) | 1.3802 | 1.3748 | 1.3711 | 1.3891 | 1.3826 | 1.4140 | 1.4084 | 1.3687 | 1.3570 |
| Cipso-Cimine (l) | 1.4358 | 1.4450 | 1.4489 | 1.4367 | 1.4411 | 1.4652 | 1.4703 | 1.4490 | 1.4674 |
| Cimine-Nimine (l) | 1.3299 | 1.3255 | 1.3266 | 1.3470 | 1.3528 | 1.3648 | 1.3702 | 1.3133 | 1.3047 |
| RMSD(Co-N only) | | 0.0378 | 0.0565 | 0.0091 | 0.0346 | 0.0697 | 0.0946 | 0.0399 | 0.0553 |
| RMSD(Co-N + ligand) | | 0.0243 | 0.0362 | 0.0112 | 0.0244 | 0.0510 | 0.0657 | 0.0270 | 0.0380 |

Table S3: Bond length analysis for $CoN_4H(MeCN)^{2+}$ obtained from the different functionals. Bonds are given in Å

| $CoN_4H(MeCN)^{2+}$ | Crystal | B3LYP-D | | BP86-D | | PBE-D | | wB97X-D | |
|---|---|---|---|---|---|---|---|---|---|
| | | M2 | M4 | M2 | M4 | M2 | M4 | M2 | M4 |
| Co1-N3 | 1.8477 | 1.8818 | 2.0318 | 1.8585 | 2.0134 | 1.9147 | 2.1107 | 1.8786 | 2.0224 |
| Co1-N4 | 1.9719 | 1.9861 | 2.1777 | 1.9599 | 2.1649 | 2.0312 | 2.1688 | 1.9860 | 2.1694 |
| Co1-N2 | 1.9663 | 1.9967 | 2.0776 | 2.0002 | 2.0684 | 2.0693 | 2.1123 | 1.9926 | 2.0731 |
| Co1-N5 | 1.9572 | 1.9869 | 2.0967 | 1.9607 | 2.0784 | 2.0313 | 2.1638 | 1.9860 | 2.0849 |
| Co1-N1 | 2.1048 | 2.0930 | 2.0336 | 2.0867 | 1.9622 | 2.1432 | 2.0897 | 2.1373 | 2.0499 |
| Nimine-Cimine (r) | 1.2940 | 1.3012 | 1.2894 | 1.3214 | 1.3039 | 1.3360 | 1.3233 | 1.2936 | 1.2835 |
| Cimine -Cipso (r) | 1.4743 | 1.4863 | 1.5041 | 1.4732 | 1.4966 | 1.5100 | 1.5323 | 1.4914 | 1.5078 |
| Cipso-Npyr (r) | 1.3449 | 1.3451 | 1.3379 | 1.3626 | 1.3499 | 1.3845 | 1.3722 | 1.3379 | 1.3320 |
| Npyr-Cipso (l) | 1.3420 | 1.3451 | 1.3422 | 1.3625 | 1.3551 | 1.3845 | 1.3723 | 1.3377 | 1.3361 |
| Cipso-Cimine (l) | 1.4755 | 1.4863 | 1.5078 | 1.4733 | 1.5022 | 1.5101 | 1.5325 | 1.4914 | 1.5113 |
| Cimine-Nimine (l) | 1.3034 | 1.3012 | 1.2928 | 1.3214 | 1.3073 | 1.3360 | 1.3234 | 1.2935 | 1.2865 |
| RMSD(Co-N only) | | 0.0281 | 0.1644 | 0.0189 | 0.1499 | 0.0776 | 0.2073 | 0.0258 | 0.1559 |
| RMSD(Co-N + ligand) | | 0.0182 | 0.1024 | 0.0180 | 0.1008 | 0.0558 | 0.1285 | 0.0201 | 0.0969 |

Table S4: Bond length analysis for $CoN_4H^{2+}$ obtained from the different functionals. Bonds are given in Å

| $CoN_4H^{2+}$ | Crystal | B3LYP-D | | BP86-D | | PBE-D | | wB97X-D | |
|---|---|---|---|---|---|---|---|---|---|
| | | M2 | M4 | M2 | M4 | M2 | M4 | M2 | M4 |
| Co1-Npyr | 1.8477 | 1.8800 | 2.0091 | 1.8624 | 1.9770 | 1.9173 | 2.0246 | 1.8743 | 2.0011 |
| Co1-Nimine (r) | 1.9719 | 1.9818 | 2.0925 | 1.9601 | 2.0291 | 2.0308 | 2.1385 | 1.9799 | 2.0867 |
| Co1-Namine | 1.9663 | 1.9816 | 2.0348 | 1.9782 | 2.0202 | 2.0463 | 2.1183 | 1.9774 | 2.0310 |
| Co1-Nimine (l) | 1.9572 | 1.9816 | 2.0931 | 1.9597 | 2.0293 | 2.0307 | 2.1370 | 1.9805 | 2.0851 |
| Nimine-Cimine (r) | 1.2940 | 1.3036 | 1.2969 | 1.3221 | 1.3199 | 1.3371 | 1.3297 | 1.2965 | 1.2904 |

*Continued on next page*

Table S4 – *Continued from previous page*

| $CoN_4H^{2+}$ | Crystal | B3LYP-D | | BP86-D | | PBE-D | | wB97X-D | |
|---|---|---|---|---|---|---|---|---|---|
| | | M2 | M4 | M2 | M4 | M2 | M4 | M2 | M4 |
| Cimine -Cipso (r) | 1.4743 | 1.4895 | 1.5050 | 1.4805 | 1.4887 | 1.5158 | 1.5398 | 1.4933 | 1.5081 |
| Cipso-Npyr (r) | 1.3449 | 1.3440 | 1.3383 | 1.3588 | 1.3564 | 1.3812 | 1.3725 | 1.3374 | 1.3323 |
| Npyr-Cipso (l) | 1.3420 | 1.3440 | 1.3383 | 1.3588 | 1.3564 | 1.3811 | 1.3726 | 1.3373 | 1.3322 |
| Cipso-Cimine (l) | 1.4755 | 1.4894 | 1.5051 | 1.4803 | 1.4885 | 1.5157 | 1.5399 | 1.4932 | 1.5080 |
| Cimine-Nimine (l) | 1.3034 | 1.3036 | 1.2968 | 1.3221 | 1.3198 | 1.3371 | 1.3298 | 1.2964 | 1.2904 |
| RMSD(Co-N only) | | 0.0222 | 0.1263 | 0.0112 | 0.0838 | 0.0709 | 0.1692 | 0.0189 | 0.1196 |
| RMSD(Co-N + ligand) | | 0.0158 | 0.0810 | 0.0148 | 0.0546 | 0.0541 | 0.1125 | 0.0150 | 0.0774 |

Table S5: Bond length analysis for $CoN_4H(MeCN)^+$ obtained from the different functionals. Bonds are given in Å

| $CoN_4H(MeCN)^+$ | Crystal | B3LYP-D | | BP86-D | | PBE-D | | wB97X-D | |
|---|---|---|---|---|---|---|---|---|---|
| | | M1 | M3 | M1 | M3 | M1 | M3 | M1 | M3 |
| Co1-N3 | 1.8074 | 1.8435 | 1.8573 | 1.8099 | 1.8599 | 1.8620 | 1.9226 | 1.8366 | 1.8491 |
| Co1-N4 | 1.9215 | 1.9580 | 1.9648 | 1.9102 | 1.9423 | 1.9872 | 2.0218 | 1.9570 | 1.9758 |
| Co1-N2 | 2.0233 | 2.0347 | 2.0183 | 2.0726 | 2.0336 | 2.1352 | 2.1197 | 2.0302 | 2.0119 |
| Co1-N5 | 1.9203 | 1.9579 | 1.9645 | 1.9101 | 1.9424 | 1.9870 | 2.0217 | 1.9566 | 1.9506 |
| Co1-N1 | 1.9987 | 2.0534 | 2.2109 | 1.9815 | 2.0439 | 2.0355 | 2.2325 | 2.1159 | 2.2840 |
| Nimine-Cimine (r) | 1.3251 | 1.3259 | 1.3298 | 1.3384 | 1.3466 | 1.3568 | 1.3604 | 1.3170 | 1.3086 |
| Cimine -Cipso (r) | 1.4350 | 1.4463 | 1.4459 | 1.4421 | 1.4449 | 1.4735 | 1.4808 | 1.4475 | 1.4622 |
| Cipso-Npyr (r) | 1.3748 | 1.3708 | 1.3709 | 1.3866 | 1.3829 | 1.4087 | 1.4078 | 1.3663 | 1.3597 |
| Npyr-Cipso (l) | 1.3689 | 1.3709 | 1.3709 | 1.3866 | 1.3830 | 1.4087 | 1.4078 | 1.3664 | 1.3703 |
| Cipso-Cimine (l) | 1.4436 | 1.4462 | 1.4458 | 1.4421 | 1.4447 | 1.4735 | 1.4807 | 1.4471 | 1.4313 |
| Cimine-Nimine (l) | 1.3188 | 1.3261 | 1.3299 | 1.3385 | 1.3468 | 1.3567 | 1.3605 | 1.3174 | 1.3339 |
| RMSD(Co-N only) | | 0.0323 | 0.0398 | 0.0258 | 0.0308 | 0.0779 | 0.1036 | 0.0295 | 0.0378 |
| RMSD(Co-N + ligand) | | 0.0259 | 0.0685 | 0.0192 | 0.0260 | 0.0549 | 0.0985 | 0.0399 | 0.0898 |

Table S6: Bond length analysis for $CoN_4H^+$ obtained from the different functionals. Bonds are given in Å

| $CoN_4H^+$ | Crystal | B3LYP-D | | BP86-D | | PBE-D | | wB97X-D | |
|---|---|---|---|---|---|---|---|---|---|
| | | M1 | M3 | M1 | M3 | M1 | M3 | M1 | M3 |
| Co1-Npyr | 1.7968 | 1.8172 | 1.8454 | 1.8130 | 1.8364 | 1.8621 | 1.8907 | 1.8079 | 1.8363 |
| Co1-Nimine (r) | 1.9116 | 1.9507 | 1.9557 | 1.9123 | 1.9318 | 1.9807 | 2.0058 | 1.9492 | 1.9543 |
| Co1-Namine | 1.9583 | 2.0054 | 2.0043 | 1.9829 | 1.9964 | 2.0583 | 2.0735 | 2.0040 | 2.0009 |
| Co1-Nimine (l) | 1.9095 | 1.9504 | 1.9551 | 1.9119 | 1.9311 | 1.9801 | 2.0052 | 1.9488 | 1.9529 |
| Nimine-Cimine (r) | 1.3228 | 1.3217 | 1.3326 | 1.3350 | 1.3508 | 1.3514 | 1.3671 | 1.3145 | 1.3235 |
| Cimine -Cipso (r) | 1.4443 | 1.4498 | 1.4447 | 1.4545 | 1.4422 | 1.4863 | 1.4742 | 1.4489 | 1.4446 |
| Cipso-Npyr (r) | 1.3680 | 1.3716 | 1.3695 | 1.3733 | 1.3806 | 1.3968 | 1.4060 | 1.3683 | 1.3650 |
| Npyr-Cipso (l) | 1.3616 | 1.3715 | 1.3695 | 1.3733 | 1.3806 | 1.3968 | 1.4060 | 1.3683 | 1.3652 |
| Cipso-Cimine (l) | 1.4502 | 1.4498 | 1.4447 | 1.4545 | 1.4422 | 1.4863 | 1.4742 | 1.4485 | 1.4437 |
| Cimine-Nimine (l) | 1.3249 | 1.3219 | 1.3328 | 1.3352 | 1.3510 | 1.3516 | 1.3674 | 1.3149 | 1.3245 |

*Continued on next page*

Table S6 – *Continued from previous page*

| $CoN_4H^+$ | Crystal | B3LYP-D | | BP86-D | | PBE-D | | wB97X-D | |
|---|---|---|---|---|---|---|---|---|---|
| | | M1 | M3 | M1 | M3 | M1 | M3 | M1 | M3 |
| RMSD(Co-N only) | | 0.0382 | 0.0461 | 0.0148 | 0.0312 | 0.0775 | 0.1002 | 0.0360 | 0.0421 |
| RMSD(Co-N + ligand) | | 0.0245 | 0.0296 | 0.0119 | 0.0244 | 0.0554 | 0.0698 | 0.0233 | 0.0267 |

Table S7: Bond length analysis for $CoN_4H$ obtained from the different functionals. Bonds are given in Å

| $CoN_4H$ | Crystal | B3LYP-D | | BP86-D | | PBE-D | | wB97X-D | |
|---|---|---|---|---|---|---|---|---|---|
| | | M2 | M4 | M2 | M4 | M2 | M4 | M2 | M4 |
| Co1-Npyr | N/A | 1.8527 | 1.8466 | 1.8105 | 1.8282 | 1.8563 | 1.8829 | 1.9473 | 1.8422 |
| Co1-Nimine (r) | N/A | 1.9062 | 1.9376 | 1.8903 | 1.9190 | 1.9560 | 1.9940 | 1.9758 | 1.9249 |
| Co1-Namine | N/A | 2.0161 | 2.0140 | 1.9979 | 2.0018 | 2.0808 | 2.0874 | 2.1176 | 2.0053 |
| Co1-Nimine (l) | N/A | 1.9058 | 1.9372 | 1.8898 | 1.9188 | 1.9557 | 1.9934 | 1.9756 | 1.9242 |
| Nimine-Cimine (r) | N/A | 1.3679 | 1.3765 | 1.3682 | 1.3910 | 1.3888 | 1.4123 | 1.3587 | 1.3713 |
| Cimine -Cipso (r) | N/A | 1.4254 | 1.4165 | 1.4261 | 1.4158 | 1.4535 | 1.4453 | 1.4339 | 1.4119 |
| Cipso-Npyr (r) | N/A | 1.3672 | 1.3679 | 1.3913 | 1.3820 | 1.4175 | 1.4063 | 1.3574 | 1.3611 |
| Npyr-Cipso (l) | N/A | 1.3672 | 1.3678 | 1.3913 | 1.3819 | 1.4175 | 1.4062 | 1.3572 | 1.3610 |
| Cipso-Cimine (l) | N/A | 1.4254 | 1.4165 | 1.4261 | 1.4158 | 1.4534 | 1.4454 | 1.4339 | 1.4119 |
| Cimine-Nimine (l) | N/A | 1.3679 | 1.3767 | 1.3684 | 1.3912 | 1.3890 | 1.4125 | 1.3587 | 1.3712 |

## 4.1 Comparison of Vibrational Spectra from experiments and Theory

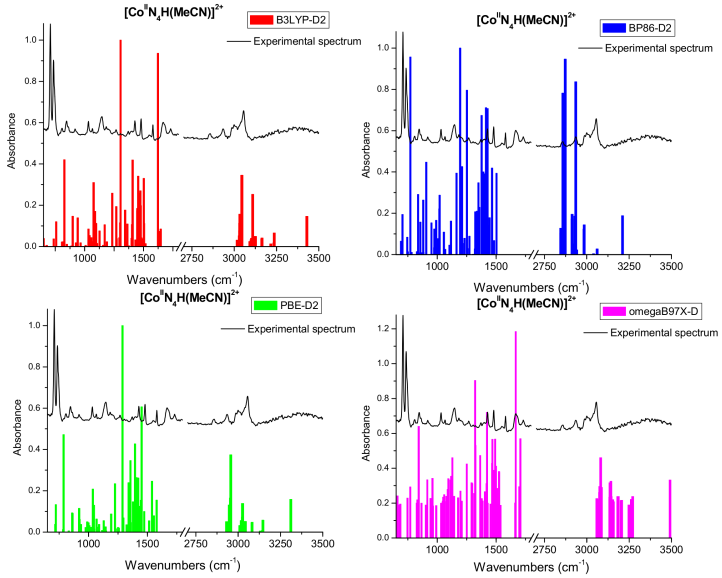



Figure S7: Basing on the characteristic 708 $cm^{-1}$ band of the Co catalyst, BP86-D2 is the most appropriate modeling method for this complex. We showed here the comparison of the different levels of theory of the shift in the ∼708±10 $cm^{-1}$ range after reduction of Co-catalyst with one electron.

# 5 Binding Modes of Substrate

We explored the binding modes that made the most chemical sense as initial guess. Thus we present in this section the optimized geometries obtained at the BP86-D level in gas phase. Then we took the most stable configuration in gas phase and used as initial guess for the solvation optimization. The most stable structures in gas phase and implicit solvation are reported in the next section.

## 5.1 $CO_2$ binding modes

### 5.1.1 $CoN_4H + CO_2$

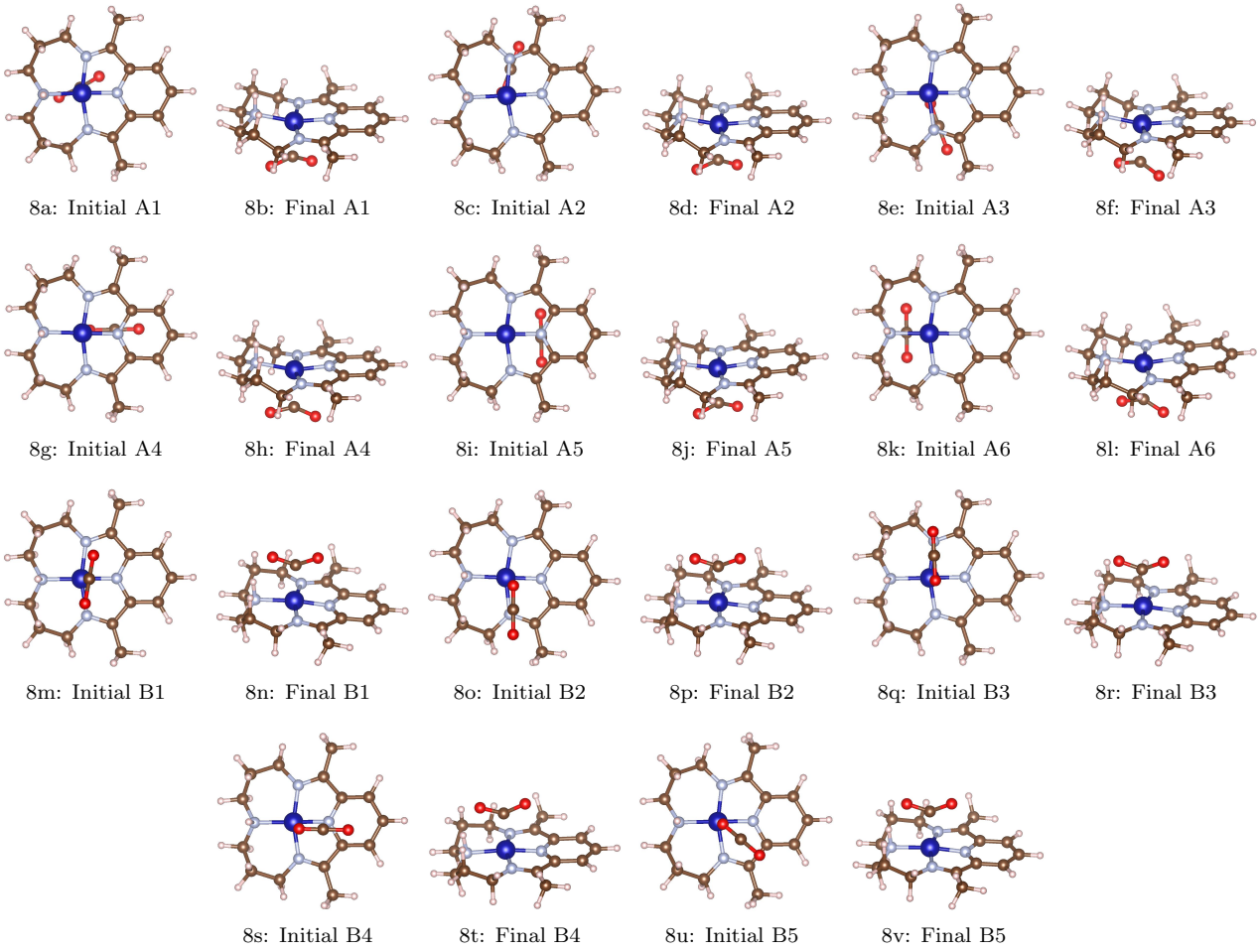



Figure S8: $CoN_4H$+$CO_2$ final Structures: Colors are C:brown, O:red, N:blue, Co:dark blue and H:pink. Initial guess for the $CO_2$ structure does not have a OCO bending, however the final optimized geometry does

Table S8: Binding energies ($\Delta G^{bind}$, kcal/mol) obtained for the different binding configurations. All other energies are in Hartree.

| Config | $E_{elec}$ | ZPE | $H_{vib}$ | $G_{vib}$ | $E_{elec}$ + ZPE | $E_{elec} + H_{vib}$ | $E_{elec} + G_{vib}$ | $\Delta G^{bind}$ |
|---|---|---|---|---|---|---|---|---|
| Site A1 | -2375.58595 | 0.35992 | 0.38300 | 0.31073 | -2375.22603 | -2375.20295 | -2375.27523 | -4.17 |
| Site A2 | -2375.58595 | 0.35997 | 0.38305 | 0.31077 | -2375.22598 | -2375.20290 | -2375.27518 | -4.11 |
| Site A3 | -2375.58602 | 0.35996 | 0.38299 | 0.31091 | -2375.22605 | -2375.20303 | -2375.27511 | -4.07 |

*Continued on next page*

Table S8 – *Continued from previous page*

| Config | $E_{\text{elec}}$ | ZPE | $H_{\text{vib}}$ | $G_{\text{vib}}$ | $E_{\text{elec}} + \text{ZPE}$ | $E_{\text{elec}} + H_{\text{vib}}$ | $E_{\text{elec}} + G_{\text{vib}}$ | $\Delta G^{bind}$ |
|---|---|---|---|---|---|---|---|---|
| Site A4 | -2375.58581 | 0.35996 | 0.38216 | 0.31237 | -2375.22585 | -2375.20365 | -2375.27344 | -3.03 |
| Site A5 | -2375.58606 | 0.36006 | 0.38307 | 0.31103 | -2375.22600 | -2375.20299 | -2375.27504 | -3.97 |
| Site A6 | -2375.58602 | 0.35999 | 0.38302 | 0.31094 | -2375.22602 | -2375.20300 | -2375.27507 | -4.03 |
| Site B1 | -2375.58735 | 0.35963 | 0.38270 | 0.31007 | -2375.22773 | -2375.20466 | -2375.27728 | -5.65 |
| Site B2 | -2375.58735 | 0.35965 | 0.38271 | 0.31010 | -2375.22771 | -2375.20464 | -2375.27726 | -5.62 |
| Site B3 | -2375.58735 | 0.35961 | 0.38270 | 0.31001 | -2375.22774 | -2375.20465 | -2375.27734 | -5.69 |
| Site B4 | -2375.58738 | 0.35968 | 0.38274 | 0.31013 | -2375.22770 | -2375.20464 | -2375.27726 | -5.59 |
| Site B5 | -2375.58737 | 0.35968 | 0.38273 | 0.31015 | -2375.22769 | -2375.20464 | -2375.27722 | -5.58 |

### 5.1.2 $CoN_4H^+ + CO_2$

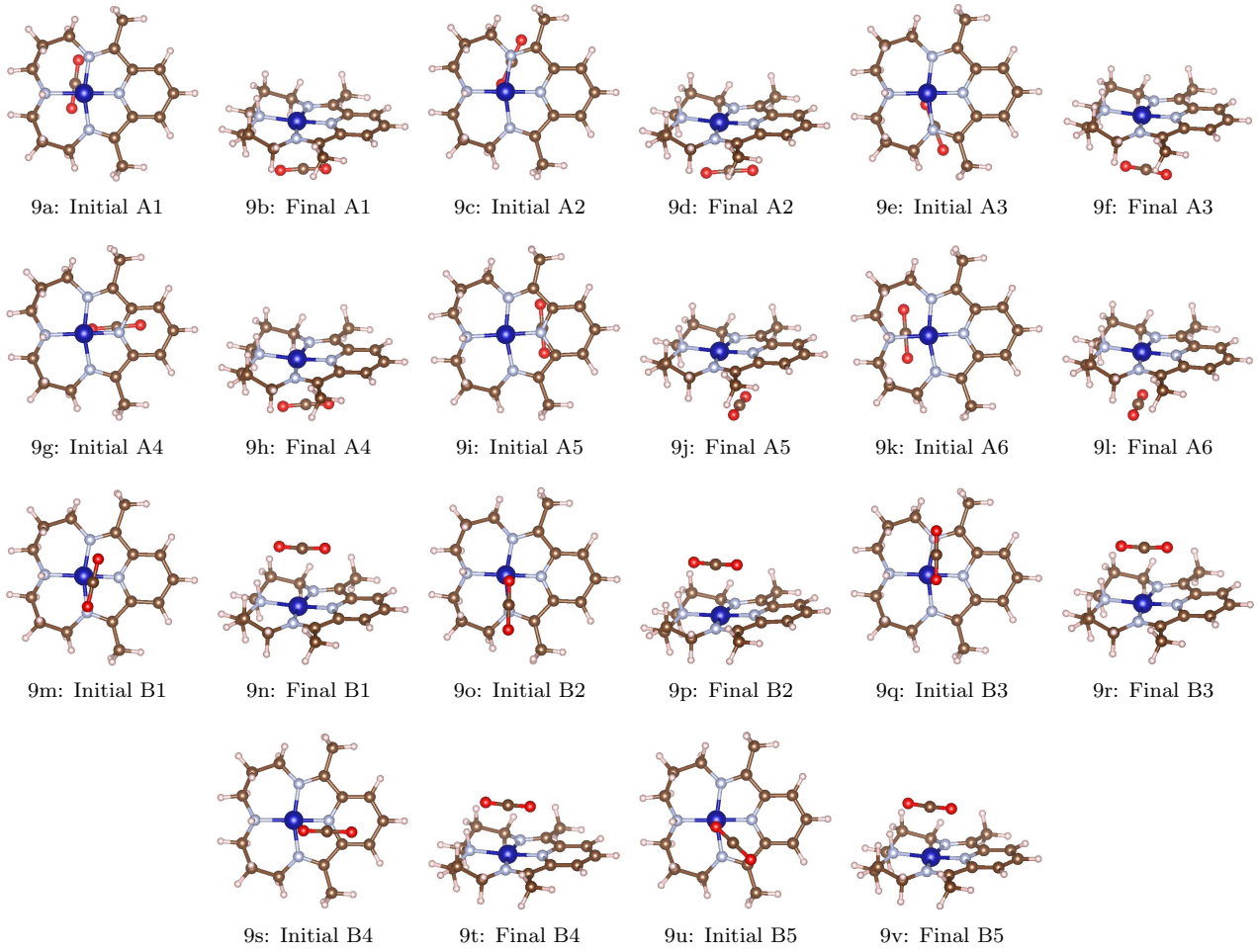



Figure S9: $CoN_4H^{+1}$+$CO_2$ final Structures for which initial guess were taken from optimized $CoN_4H$ + $CO_2$: Colors are C:brown, O:red, N:blue, Co:dark blue and H:pink.

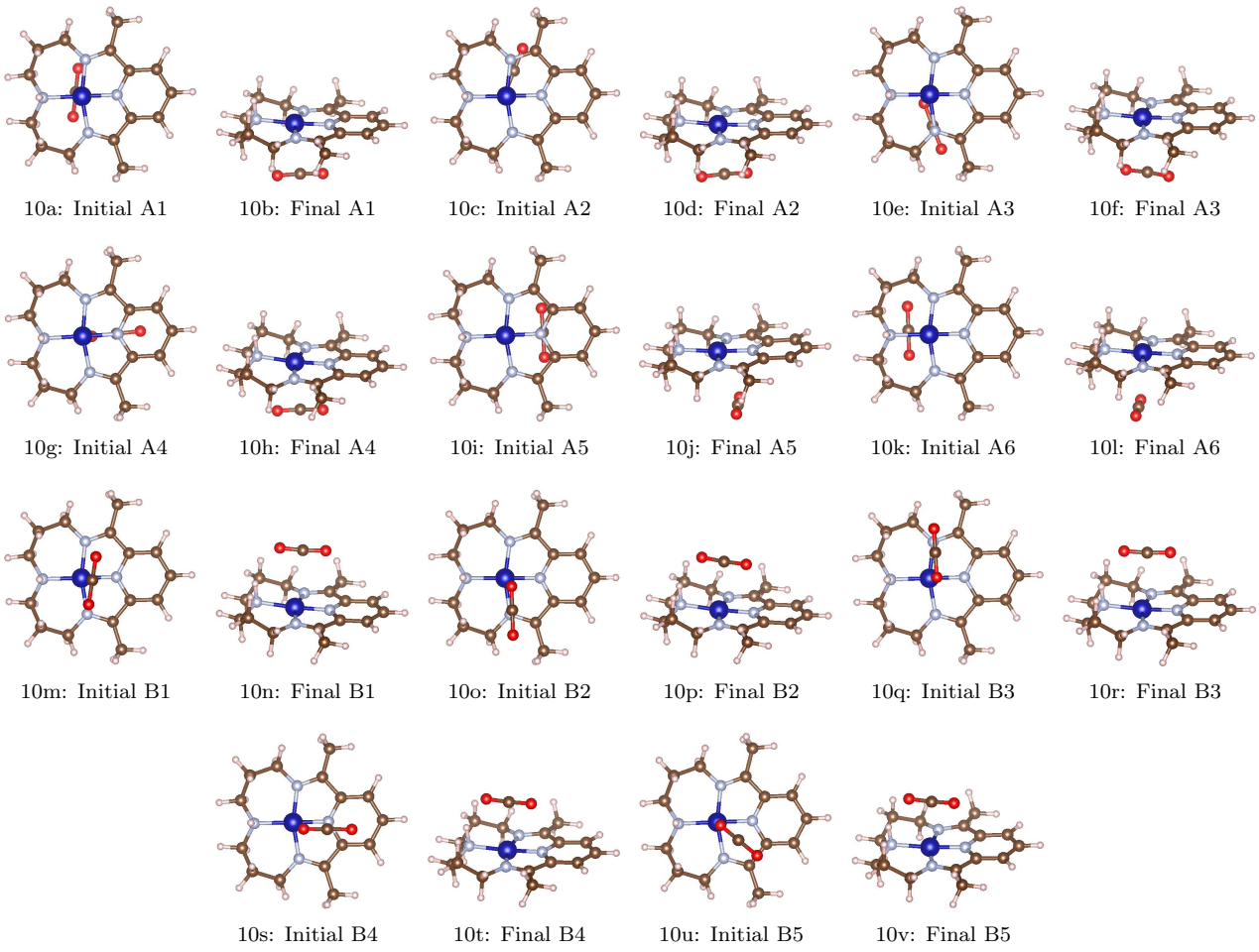
Table S9: Binding energies ($\Delta G^{bind}$, kcal/mol) obtained for the different binding configurations. All other energies are in Hartree.

| Config | $E_{elec}$ | ZPE | $H_{vib}$ | $G_{vib}$ | $E_{elec}$ + ZPE | $E_{elec} + H_{vib}$ | $E_{elec} + G_{vib}$ | $\Delta G^{bind}$ |
|---|---|---|---|---|---|---|---|---|
| Initial guess taken from optimized CoN4H + bended $CO_2$ bended | | | | | | | | |
| Site A1 | -2375.40804 | 0.36281 | 0.38583 | 0.31336 | -2375.04523 | -2375.02222 | -2375.09468 | 3.49 |
| Site A2 | -2375.40806 | 0.36291 | 0.38589 | 0.31358 | -2375.04515 | -2375.02218 | -2375.09448 | 3.68 |
| Site A3 | -2375.40802 | 0.36269 | 0.38577 | 0.31299 | -2375.04533 | -2375.02226 | -2375.09503 | 3.20 |
| Site A4 | -2375.40803 | 0.36278 | 0.38583 | 0.31319 | -2375.04525 | -2375.02220 | -2375.09484 | 3.38 |
| Site A5 | -2375.40803 | 0.36275 | 0.38581 | 0.31313 | -2375.04528 | -2375.02222 | -2375.09490 | 3.32 |
| Site A6 | -2375.40804 | 0.36283 | 0.38584 | 0.31340 | -2375.04521 | -2375.02221 | -2375.09464 | 3.53 |
| Site B1 | -2375.40308 | 0.36190 | 0.38450 | 0.31294 | -2375.04119 | -2375.01859 | -2375.09015 | 5.77 |
| Site B2 | -2375.40310 | 0.36195 | 0.38547 | 0.30977 | -2375.04115 | -2375.01762 | -2375.09332 | 3.81 |
| Site B3 | -2375.40307 | 0.36182 | 0.38445 | 0.31278 | -2375.04125 | -2375.01862 | -2375.09029 | 5.63 |

*Continued on next page*

Table S9 – *Continued from previous page*

| Config | $E_{\text{elec}}$ | ZPE | $H_{\text{vib}}$ | $G_{\text{vib}}$ | $E_{\text{elec}} + \text{ZPE}$ | $E_{\text{elec}} + H_{\text{vib}}$ | $E_{\text{elec}} + G_{\text{vib}}$ | $\Delta G^{bind}$ |
|---|---|---|---|---|---|---|---|---|
| Site B4 | -2375.40312 | 0.36197 | 0.38550 | 0.30966 | -2375.04115 | -2375.01762 | -2375.09346 | 3.74 |
| Site B5 | -2375.40311 | 0.36199 | 0.38550 | 0.31007 | -2375.04113 | -2375.01762 | -2375.09304 | 4.01 |
| Initial guess taken from $CoN_4H^{+1}$ + planar $CO_2$ planar | | | | | | | | |
| Site A1 | -2375.40382 | 0.36162 | 0.38559 | 0.30874 | -2375.04219 | -2375.01822 | -2375.09507 | 2.50 |
| Site A2 | -2375.40381 | 0.36156 | 0.38557 | 0.30846 | -2375.04226 | -2375.01824 | -2375.09535 | 2.29 |
| Site A3 | -2375.40382 | 0.36142 | 0.38547 | 0.30819 | -2375.04241 | -2375.01835 | -2375.09563 | 2.02 |
| Site A4 | -2375.40382 | 0.36140 | 0.38551 | 0.30808 | -2375.04242 | -2375.01831 | -2375.09574 | 1.95 |
| Site A5 | -2375.40274 | 0.36135 | 0.38553 | 0.30620 | -2375.04139 | -2375.01721 | -2375.09654 | 1.41 |
| Site A6 | -2375.40285 | 0.36160 | 0.38466 | 0.31099 | -2375.04126 | -2375.01819 | -2375.09186 | 4.50 |
| Site B1 | -2375.40429 | 0.36171 | 0.38567 | 0.30882 | -2375.04258 | -2375.01861 | -2375.09547 | 2.31 |
| Site B2 | -2375.40432 | 0.36180 | 0.38572 | 0.30925 | -2375.04252 | -2375.01861 | -2375.09507 | 2.62 |
| Site B3 | -2375.40426 | 0.36156 | 0.38560 | 0.30790 | -2375.04270 | -2375.01866 | -2375.09636 | 1.66 |
| Site B4 | -2375.40429 | 0.36175 | 0.38571 | 0.30879 | -2375.04254 | -2375.01858 | -2375.09550 | 2.31 |
| Site B5 | -2375.40432 | 0.36177 | 0.38571 | 0.30888 | -2375.04255 | -2375.01860 | -2375.09544 | 2.37 |



10a: Initial A1 10b: Final A1 10c: Initial A2 10d: Final A2 10e: Initial A3 10f: Final A3

10g: Initial A4 10h: Final A4 10i: Initial A5 10j: Final A5 10k: Initial A6 10l: Final A6

10m: Initial B1 10n: Final B1 10o: Initial B2 10p: Final B2 10q: Initial B3 10r: Final B3

10s: Initial B4 10t: Final B4 10u: Initial B5 10v: Final B5

Figure S10: $CoN_4H^{+1}$+$CO_2$ final Structures for which Initial guess were taken from $CoN_4H^{+1}$ + planar $CO_2$: Colors are C:brown, O:red, N:blue, Co:dark blue and H:pink.

# 6 Geometries of the most stable $CO_2$ binding modes

Note that all atoms the final structures are given in the standard x,y,z format:

```
Atom  X  Y  Z
Atom1 X1 Y1 Z1
Atom2 X2 Y2 Z2
...
```

## 6.1 Gas phase

### 6.1.1 $CoN_4H^{+1}$ — $CO_2$ (BP86, bottom)

```
Co  0.72715 13.09470  6.04987
N -0.38965 14.44518  6.81592
N  1.90453 11.60671  5.81694
N  0.64994 12.43863  7.73925
N  0.69267 13.72491  4.17083
C  2.71657 11.31250  4.62536
C -0.68582 14.29194  8.10625
C  1.86028 13.33671  3.31414
C  1.34066 11.29381  8.05189
C -0.21056 12.57748  9.99017
C -0.10894 13.08665  8.68265
C -0.95361 15.54196  4.64566
C -1.47457 15.27484  8.92224
C  0.48184 11.39638 10.31615
C  2.10064 10.84665  6.89438
C  2.07876 11.82499  3.33272
C  0.35613 15.16976  3.95339
C  3.05145  9.68660  6.95657
C  1.26948 10.74809  9.34661
H -0.81687 13.09414 10.73829
H  0.41251 10.98468 11.32689
H  1.81916  9.83615  9.59221
H -0.11574 13.19025  3.80319
H  3.70356 11.79950  4.76758
H  2.89572 10.22626  4.53291
H  1.66875 13.68395  2.28010
H  2.74711 13.87258  3.69679
H -1.73044 14.78973  4.40472
H -2.50245 15.39100  8.52933
H -1.54517 14.95088  9.97092
H  2.74592 11.55575  2.49531
H  1.11600 11.30680  3.15366
H  0.28010 15.35262  2.86374
H  2.75591  8.88482  6.25337
H  4.07367 10.00588  6.68132
H  3.08511  9.25741  7.96868
H -1.30534 16.50596  4.23836
C -0.82429 15.68968  6.16265
H -0.99828 16.27254  8.89888
H  1.19722 15.77012  4.34347
H -1.79006 16.03267  6.57515
H -0.06935 16.46901  6.39507
O  3.80320 13.56973  7.31582
C  3.06649 14.45566  7.58517
O  2.38029 15.37264  7.88284
```

### 6.1.2 $CoN_4H^{+1}$ — $CO_2$ (BP86, top)

```
Co  0.76258 13.19359  6.04252
N -0.33714 14.56268  6.80147
N  1.89893 11.67510  5.80294
N  0.73788 12.58548  7.75074
N  0.65072 13.76058  4.14502
C  2.62735 11.30177  4.57724
C -0.59358 14.44297  8.10590
C  1.77876 13.32932  3.26047
C  1.41400 11.43423  8.06733
C -0.07240 12.77422 10.01609
C  0.00627 13.25707  8.69732
C -0.98761 15.57745  4.61005
C -1.38811 15.43115  8.91049
C  0.61193 11.59076 10.34874
C  2.11766 10.93818  6.89411
C  1.94968 11.81095  3.30331
C  0.31385 15.19920  3.90316
C  3.01867  9.73769  6.94343
C  1.36486 10.91210  9.37274
H -0.65935 13.30993 10.76628
H  0.55934 11.19791 11.36792
H  1.90130  9.99283  9.62072
H -0.17741 13.21940  3.83796
H  3.64811 11.73197  4.64540
H  2.73893 10.20437  4.51191
H  1.56203 13.65940  2.22579
H  2.69331 13.84703  3.60106
H -1.75558 14.80721  4.40401
H -2.44316 15.46278  8.57639
H -1.37716 15.16944  9.97875
H  2.56950 11.49921  2.44457
H  0.96230 11.32492  3.17870
H  0.21523 15.35899  2.81173
H  2.62662  8.91669  6.31256
H  4.02809  9.98500  6.56669
H  3.11658  9.36024  7.97193
H -1.36001 16.52558  4.18448
C -0.83345 15.77126  6.11987
H -0.97954 16.45213  8.79815
H  1.16058 15.81027  4.26392
H -1.80411 16.08584  6.54415
H -0.10998 16.59057  6.31228
O -1.91338 12.01605  4.63394
C -1.90766 11.74157  5.78981
O -1.98655 11.43027  6.92556
```

### 6.1.3 $CoN_4H$ — $CO_2$ (BP86, bottom)

```
Co  0.89958 13.24686  6.03839
N -0.31189 14.53124  6.74849
N  2.04848 11.75613  5.80377
N  0.73414 12.53138  7.69807
N  0.63868 13.71419  4.08126
C  2.86087 11.53642  4.60714
C -0.59125 14.39421  8.06386
C  1.69087 13.25855  3.12661
C  1.47670 11.41026  8.02344
```

```
C -0.07614 12.72749  9.95770
C -0.00640 13.21819  8.64233
C -0.91458 15.60381  4.58340
C -1.38043 15.39233  8.86679
C  0.63325 11.55703 10.29658
C  2.24361 10.97485  6.88996
C  2.05563 11.78784  3.32435
C  0.33595 15.15225  3.82798
C  3.19247  9.80752  6.93835
C  1.42116 10.89702  9.33073
H -0.66349 13.25899 10.71218
H  0.58922 11.17062 11.31944
H  1.99814 10.00628  9.59639
H -0.21771 13.18516  3.84780
H  3.71049 12.24898  4.63894
H  3.26937 10.50927  4.58437
H  1.32853 13.43303  2.09168
H  2.57075 13.89546  3.31366
H -1.73804 14.88139  4.40799
H -2.39968 15.54020  8.45909
H -1.48045 15.05315  9.90969
H  2.66759 11.46995  2.45994
H  1.14214 11.15933  3.32959
H  0.19528 15.30475  2.73683
H  2.93239  9.03236  6.19093
H  4.23379 10.12373  6.73510
H  3.16825  9.33731  7.93403
H -1.24153 16.57408  4.16674
C -0.69998 15.78013  6.08988
H -0.88073 16.38027  8.87597
H  1.22841 15.71417  4.15360
H -1.62622 16.19272  6.53300
H  0.10677 16.52507  6.25687
O  3.07015 14.70611  5.41439
C  2.48383 14.51076  6.49732
O  2.56251 14.84681  7.67649
```

### 6.1.4 $CoN_4H$ — $CO_2$ (BP86, top)

```
Co  0.59843 13.10427  6.03178
N -0.43709 14.51048  6.78635
N  1.75999 11.61806  5.79477
N  0.72911 12.60445  7.78103
N  0.66403 13.79965  4.15124
C  2.41770 11.17015  4.55965
C -0.64058 14.43213  8.12223
C  1.82156 13.34932  3.34368
C  1.42207 11.45380  8.09292
C  0.02186 12.87629 10.06663
C  0.01357 13.30637  8.72795
C -0.99633 15.56519  4.58216
C -1.45019 15.43187  8.89930
C  0.74909 11.71841 10.41065
C  2.03635 10.90957  6.91451
C  1.84455 11.81639  3.29664
C  0.38558 15.24676  3.99752
C  2.91307  9.68896  6.93029
C  1.45056 10.99748  9.42262
H -0.53913 13.42931 10.82574
H  0.75956 11.37079 11.44825
H  2.00123 10.08808  9.68060
H -0.17741 13.27985  3.81129
H  3.50238 11.40591  4.63129
H  2.33660 10.06971  4.46114
H  1.72847 13.76081  2.31645
H  2.74947 13.75367  3.79275
H -1.70323 14.77419  4.26766
H -2.51118 15.42999  8.57911
H -1.41912 15.20269  9.97603
H  2.45815 11.48595  2.43917
H  0.81258 11.45294  3.13124
H  0.41243 15.50808  2.91844
H  2.46817  8.86316  6.33999
H  3.90858  9.89882  6.49293
H  3.05887  9.33021  7.96131
H -1.35759 16.52309  4.16640
C -1.00674 15.68229  6.10747
H -1.07097 16.46219  8.75375
H  1.18249 15.82040  4.50947
H -2.04959 15.84859  6.44206
H -0.42677 16.58238  6.40867
O -1.43619 12.12183  4.40348
C -1.11886 11.94195  5.60350
O -1.51666 11.29886  6.56749
```

## 6.2 Implicit Solvent ($CH_3CN$)

### 6.2.1 $CoN_4H^{+1}$ — $CO_2$ (BP86, bottom)

```
Co  0.73524 13.10037  6.05231
N -0.38164 14.44971  6.81720
N  1.90995 11.61189  5.81848
N  0.65886 12.44525  7.74138
N  0.69280 13.72477  4.17295
C  2.71542 11.31247  4.62345
C -0.68283 14.29431  8.10609
C  1.85844 13.33610  3.31506
C  1.34751 11.29790  8.05319
C -0.20858 12.58043  9.99082
C -0.10398 13.09151  8.68400
C -0.95088 15.54105  4.64583
C -1.48547 15.26996  8.91672
C  0.48392 11.39843 10.31599
C  2.10443 10.84995  6.89477
C  2.07366 11.82468  3.33370
C  0.35920 15.16946  3.95562
C  3.04713  9.68338  6.95237
C  1.27300 10.74976  9.34692
H -0.81723 13.09614 10.73756
H  0.41282 10.98552 11.32616
H  1.82088  9.83643  9.59101
H -0.11623 13.19293  3.80387
H  3.70360 11.79767  4.76029
H  2.89024 10.22576  4.53412
H  1.66083 13.68089  2.28216
H  2.74624 13.87200  3.69418
H -1.72634 14.78831  4.40465
H -2.51670 15.35883  8.52586
H -1.54250 14.95485  9.96892
H  2.73962 11.55429  2.49614
H  1.10963 11.30879  3.15851
H  0.28161 15.34859  2.86627
H  2.73477  8.88245  6.25588
H  4.06720  9.99280  6.65953
H  3.08898  9.26034  7.96680
H -1.30110 16.50563  4.23948
C -0.82274 15.69117  6.16178
H -1.03184 16.27720  8.87675
H  1.20059 15.76915  4.34478
H -1.78935 16.02910  6.57513
H -0.07055 16.47316  6.39245
O  3.81918 13.57409  7.33081
C  3.07539 14.45601  7.59494
O  2.39651 15.37543  7.90252
```

### 6.2.2 $CoN_4H^{+1}$ — $CO_2$ (BP86, top)

```
Co  0.75674 13.18115  6.03541
N -0.34833 14.54563  6.79106
N  1.89649 11.66561  5.79718
N  0.73709 12.57738  7.74476
N  0.65638 13.75277  4.14034
C  2.62790 11.28999  4.57366
C -0.59922 14.43156  8.09684
C  1.79999 13.33262  3.27035
C  1.41825 11.42895  8.06278
C -0.06325 12.77517 10.01373
C  0.00793 13.25202  8.69199
C -0.98745 15.56466  4.59774
C -1.39601 15.42024  8.89678
C  0.62609 11.59406 10.34744
C  2.11933 10.93191  6.88895
C  1.96768 11.81444  3.29822
C  0.32485 15.19446  3.90864
C  3.02427  9.73535  6.93756
C  1.37637 10.91185  9.37078
H -0.64694 13.31446 10.76376
H  0.58018 11.20591 11.36885
H  1.91766  9.99572  9.61920
H -0.16489 13.21773  3.80736
H  3.65263 11.70701  4.65335
H  2.72486 10.19192  4.50472
H  1.59774 13.67460  2.23741
H  2.70790 13.84572  3.63325
H -1.75056 14.79497  4.37529
H -2.45088 15.44144  8.56243
H -1.37878 15.16652  9.96680
H  2.60022 11.51177  2.44600
H  0.98183 11.33139  3.15434
H  0.24306 15.36266  2.81785
H  2.63472  8.91735  6.30191
H  4.03129  9.99021  6.55982
H  3.12159  9.35633  7.96543
H -1.35351 16.51605  4.17482
C -0.85738 15.74966  6.10958
H -0.99345 16.44168  8.77008
H  1.16593 15.80004  4.28962
H -1.83911 16.04058  6.52369
H -0.15124 16.57901  6.31921
O -2.02981 12.16172  4.72267
C -1.95350 11.82708  5.85915
O -1.98577 11.44397  6.97685
```

### 6.2.3 $CoN_4H$ — $CO_2$ (BP86, bottom)

```
Co  0.95278 13.29023  6.05485
N -0.25900 14.57692  6.76725
N  2.08442 11.78013  5.81314
N  0.75508 12.55448  7.70505
N  0.65252 13.72142  4.09777
C  2.87348 11.53176  4.60315
C -0.57364 14.41933  8.06935
C  1.69950 13.26557  3.13638
C  1.48989 11.42748  8.02732
C -0.07900 12.73513  9.95806
C  0.00700 13.23649  8.64716
C -0.93129 15.58889  4.59182
C -1.41934 15.38276  8.85824
C  0.62522 11.55918 10.29427
C  2.25794 10.98841  6.89151
C  2.05880 11.79366  3.32997
C  0.30937 15.14629  3.81681
C  3.17153  9.79289  6.93149
C  1.42144 10.90383  9.33016
H -0.67788 13.25778 10.70957
H  0.56653 11.16202 11.31212
H  1.98844 10.00617  9.59333
H -0.19473 13.17053  3.88046
H  3.74377 12.21853  4.61789
H  3.25592 10.49602  4.58526
H  1.32795 13.43766  2.10636
H  2.58072 13.90327  3.31446
H -1.74416 14.84878  4.45181
H -2.43799 15.47267  8.43438
H -1.51616 15.04632  9.90203
H  2.66329 11.47220  2.46279
H  1.14221 11.17137  3.33812
H  0.13548 15.26324  2.72807
H  2.87229  9.02657  6.19096
```

```
H  4.21656 10.07627  6.70476
H  3.15089  9.32645  7.92855
H -1.28649 16.54340  4.16414
C -0.68310 15.80621  6.08750
H -0.97662 16.39665  8.86228
H  1.19500 15.73869  4.10393
H -1.60152 16.21431  6.54650
H  0.11669 16.56506  6.21493
O  3.05575 14.83756  5.41955
C  2.51987 14.48013  6.49747
O  2.75106 14.70493  7.70013
```

### 6.2.4 $CoN_4H$ — $CO_2$ (BP86, top)

```
Co  0.54707 13.06857  6.01925
N -0.46904 14.49416  6.78214
N  1.73285 11.59155  5.78724
N  0.69835 12.58232  7.77340
N  0.64738 13.78641  4.14952
C  2.40038 11.14962  4.55184
C -0.65778 14.42424  8.11697
C  1.82693 13.34581  3.36241
C  1.40839 11.44313  8.08854
C  0.02494 12.87903 10.06646
C -0.00266 13.29474  8.72327
C -0.99277 15.57561  4.57875
C -1.43615 15.44382  8.89928
C  0.76192 11.72629 10.41235
C  2.02565 10.89779  6.90783
C  1.85140 11.81548  3.28967
C  0.39377 15.24356  4.01708
C  2.93695  9.70350  6.93003
C  1.45769 10.99997  9.42237
H -0.52056 13.44247 10.82896
H  0.79184 11.39224 11.45385
H  2.02565 10.10258  9.68411
H -0.18486 13.28966  3.76653
H  3.48373 11.37598  4.64328
H  2.31251 10.05105  4.44675
H  1.75713 13.77555  2.34291
H  2.74164 13.74320  3.84117
H -1.70725 14.80335  4.23630
H -2.49466 15.47852  8.57552
H -1.41261 15.21298  9.97537
H  2.48412 11.49991  2.44180
H  0.82448 11.45398  3.09238
H  0.44724 15.51958  2.94468
H  2.52713  8.87132  6.32498
H  3.92817  9.95034  6.50383
H  3.08243  9.34168  7.95952
H -1.32982 16.54479  4.17142
C -1.02947 15.67422  6.10383
H -1.02346 16.46023  8.75182
H  1.19033 15.79254  4.55363
H -2.07500 15.83708  6.42919
H -0.45211 16.56643  6.42589
O -1.47652 12.08813  4.40384
C -1.11936 11.95512  5.60901
O -1.57709 11.29683  6.55863
```

# Bibliography

[1] D. C. Lacy, C. C. L. McCrory, and J. C. Peters, "Studies of Cobalt-Mediated Electrocatalytic CO2 Reduction Using a Redox-Active Ligand," *Inorganic Chemistry*, vol. 53, pp. 4980–4988, MAY 19 2014.

[2] G. M. Sheldrick, "A short history of SHELX," *Acta Crystallographica Section A*, vol. 64, pp. 112–122, JAN 2008.

[3] O. Dolomanov, A. Blake, N. Champness, and M. Schroder, "OLEX: new software for visualization and analysis of extended crystal structures," *Journal of Applied Crystallography*, vol. 36, pp. 1283–1284, OCT 2003.

[4] Y. Shao, Z. Gan, E. Epifanovsky, A. T. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Ku, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. Hanson-Heine, P. H. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. ONeill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stck, Y.-C. Su, A. J. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. Gill, and M. Head-Gordon, "Advances in molecular quantum chemistry contained in the q-chem 4 program package," *Molecular Physics*, pp. 1–32, DOI: 10.1080/00268976.2014.952696, http://dx.doi.org/10.1080/00268976.2014.952696.

[5] J. Wachters *Journal of Chemical Physics*, vol. 52, p. 1033, 1970.

[6] C. W. Bauschlicher, S. R. Langhoff, and L. A. Barnes *Journal of Chemical Physics*, vol. 91, p. 2399, 1989.

[7] A. W. Lange and J. M. Herbert *Journal of Chemical Physics*, vol. 133, DEC 28 2010.

[8] A. W. Lange and J. M. Herbert *Chemical Physics Letters*, vol. 509, pp. 77–87, JUN 3 2011.